

## PATENT SPECIFICATION

661184



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SPECIFICATION NO. 661184

INVENTORS: - DERRICK JOHN FENNE and MARTIN ISRAEL MUGDAN deceased

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of The Distillers Company Limited, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland.

THE PATENT OFFICE,  
1st March, 1952

DS 11031/1(5)/3295 150 3/52 R

1 I, DERRICK JOHN FENNE, of 42, Mount Ararat Road, Richmond, Surrey, do hereby declare the nature of this invention to be as follows:—

15 The present invention relates to the manufacture of acetal condensation products.

It is known that di-acetals of the formula  $R.O.CH.O.CH.O.R.$ , in which "R"

20  $\begin{array}{c} CH_3 \quad CH_3 \\ | \quad | \\ CH_2 \quad CH_2 \end{array}$  stands for the methyl or ethyl group, can be prepared by reacting bis- (alpha chlor ethyl) ether with a solution of metallic sodium in methanol or ethanol (Geuther and Laatsch, Ann. 218, 1883, page 25).

25 It is an object of the present invention to produce poly-acetals by which term are to be understood compounds of the general formula

30  $C_2H_5O.[CH(CH_3)_2O]_n.C_2H_5$  in which "n" is a numeral higher than 1, in particular 2 and 3, in a simple and less circuitous manner.

The process of producing poly-acetals of the above given general formula comprises adding a small amount of acid to a mixture of acetal and acetaldehyde at a temperature between  $+20^\circ$  and  $-50^\circ$  C.

40 As acids may be used hydrogen halogenides, such as hydrochloric acid or hydrobromic acid, sulphuric acid or mono alkylated sulphuric acids, such as methyl hydrogen sulphate. The quantity of acid to be added can vary within very wide limits and depends partly on whether the intention is to produce the di-acetal, the tri-acetal or higher acetals, and also on the temperature in the reaction mixture.

[P]

some cases, as little as 0.001 mol per cent or even less was found to be sufficient. 60 It is desirable to add the acid in a diluted form in order to avoid too great an increase of temperature as this may give rise to very violent reactions which might even assume an explosive character. As 65 diluent for the acid such substances as ethyl ether or alcohol may be used with advantage. Thus, for instance, the hydrogen halides are applied dissolved in ethyl ether and the sulphuric acid diluted 70 with ethanol or methanol. Care has to be taken, also, to cool the reaction mixture efficiently in order to maintain the temperature within the desired range. 75 The molar ratio of acetal to acetaldehyde may also vary within wide limits; ratios of acetal to aldehyde from 2:1 to 1:6 may for instance be used. A predominance of acetaldehyde will lead to the preferential formation of poly acetals 80 favoured by effecting the reaction at the lower temperatures. A molar ratio of acetal to acetaldehyde of 2:1, on the other hand, leads to the production of a mixture which contains more di-acetal than 85 tri and poly acetals.

When the reaction was carried out at temperatures of  $-50^\circ$  C. and lower, it was found that with the formation of the poly-acetals increasing quantities of the auto-condensation products of acetaldehyde 90 were formed. Small amounts of these latter substances were formed besides the production of poly-acetals when the reaction was carried out according to the process of the invention. 95

The separation of the polyacetals from

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## PROVISIONAL SPECIFICATION

### Manufacture of Poly-Acetals

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, Scotland, DERRICK JOHN FENNE, a British Subject, of the Company's Research & Development Dept., Great Burgh, Epsom, Surrey, and MAGDALENA SARAH MUGDAN, a British Subject, of 42, Mount Ararat Road, Richmond, Surrey, the Legal Representative of MARTIN ISRAEL MUGDAN, Deceased, late a British Subject, of 42, Mount Ararat Road, Richmond, Surrey, do hereby declare the nature of this invention to be as follows:—

The present invention relates to the manufacture of acetal condensation products.

It is known that di-acetals of the formula  $R.O.CH.O.CH.O.R.$ , in which "R"

$CH_3$ ,  $CH_2$  stands for the methyl or ethyl group, can be prepared by reacting bis- (alpha chlor ethyl) ether with a solution of metallic sodium in methanol or ethanol (Geuther and Laatsch, Ann. 218, 1883, page 25).

It is an object of the present invention to produce poly-acetals by which term are to be understood compounds of the general formula

$C_2H_5O.[—CH(CH_3)—O]_n—C_2H_5$  in which "n" is a numeral higher than 1, in particular 2 and 3, in a simple and less circuitous manner.

The process of producing poly-acetals of the above given general formula comprises adding a small amount of acid to a mixture of acetal and acetaldehyde at a temperature between  $+20^\circ$  and  $-50^\circ$  C.

As acids may be used hydrogen halogenides, such as hydrochloric acid or hydrobromic acid, sulphuric acid or mono alkylated sulphuric acids, such as methyl hydrogen sulphate. The quantity of acid to be added can vary within very wide limits and depends partly on whether the intention is to produce the di-acetal, the tri-acetal or higher acetals, and also on the temperature in the reaction mixture.

[P]

The higher the temperature within the indicated limits the smaller can be the quantity of acid to be added. It has been found that at temperatures above zero a trace of the acid is sufficient to produce the desired effect. At the lower temperature as much as 0.5 mol per cent. based on whatever reacting component of the initial reaction mixture is present in the smaller quantity, may be used but in some cases, as little as 0.001 mol per cent or even less was found to be sufficient. It is desirable to add the acid in a diluted form in order to avoid too great an increase of temperature as this may give rise to very violent reactions which might even assume an explosive character. As diluent for the acid such substances as ethyl ether or alcohol may be used with advantage. Thus, for instance, the hydrogen halides are applied dissolved in ethyl ether and the sulphuric acid diluted with ethanol or methanol. Care has to be taken, also, to cool the reaction mixture efficiently in order to maintain the temperature within the desired range. The molar ratio of acetal to acetaldehyde may also vary within wide limits; ratios of acetal to aldehyde from 2:1 to 1:6 may for instance be used. A predominance of acetaldehyde will lead to the preferential formation of poly acetals favoured by effecting the reaction at the lower temperatures. A molar ratio of acetal to acetaldehyde of 2:1, on the other hand, leads to the production of a mixture which contains more di-acetal than tri and poly acetals.

When the reaction was carried out at temperatures of  $-50^\circ$  C. and lower, it was found that with the formation of the poly-acetals increasing quantities of the auto-condensation products of acetaldehyde were formed. Small amounts of these latter substances were formed besides the production of poly-acetals when the reaction was carried out according to the process of the invention.

The separation of the polynacetals from

- metaldehyde, paraldehyde and unreacted acetal and acetaldehyde can be carried out by fractional distillation after the reaction mixture has been neutralised. The diacetal boils at 156.5 to 158.5° C. at ordinary pressure, while the triacetal has a boiling point of 84 to 89° C. at 5 mm pressure and a refractive index  $n_D^{20} = 1.4087$ .
- The following examples illustrate the manner in which the process of the invention may be carried out in practice.

#### EXAMPLE 1

- Freshly distilled acetal (b.p. 103—104° C.) was mixed in equimolecular proportion with freshly distilled acetaldehyde and to 50 cc of the mixture cooled to -45° C. was added 0.01 mol % of sulphuric acid (based on the initial acetaldehyde) diluted with methanol. The reaction mixture was kept at -45° C. for two hours then neutralised and subjected to fractional distillation. 28% of the initial acetaldehyde were converted to di-acetal and tri-acetal and 9.3% to paraldehyde and metaldehyde.

#### EXAMPLE 2

- Acetal and acetaldehyde were mixed in a molar proportion of 2:1. 0.1 mol % of methyl hydrogen sulphate (based on the initial acetaldehyde) diluted with methanol was added at -20° C. After

two hours and treatment as indicated in Example 1, 40% of the acetaldehyde were converted to di-acetal and poly-acetal.

#### EXAMPLE 3

When 0.1 mol % of methyl hydrogen sulphate was added to a mixture, as used in Example 2, at a temperature of 15° C. di-acetal in a yield of 15% (based on the initial acetaldehyde) was obtained after  $\frac{1}{2}$  hour.

#### EXAMPLE 4

To a mixture of one mol of acetal and 6 mols of acetaldehyde was added 0.002 mol % of methyl hydrogen sulphate (based on the initial acetal) diluted with methanol at a temperature of -40° C. After 1½ hours and neutralisation the reaction mixture yielded on fractionation 16.9 cc of a mixture boiling between 128° C. and 180° C. and consisting mainly of di-acetal and some tri-acetal, and 15.0 cc of a poly-acetal of the above given general formula, wherein "n" is 3 and greater than 3.

The poly acetals produced according to the process of the invention may be used, e.g. as froth flotation agents and as organic intermediates.

Dated this 29th day of October, 1948.

N. F. BAKER,

Agent for the Applicants.

### COMPLETE SPECIFICATION

#### Manufacture of Poly-Acetals

- We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, Scotland, DERRICK JOHN FENNE, a British Subject, of the Company's Research & Development Dept., Great Burgh, Epsom, Surrey, and MAGDALENA SARAH MUGDAN, a British Subject, of 42, Mount Ararat Road, Richmond, Surrey, the Legal Representative of MARTIN ISRAEL MUGDAN, Deceased, late a British Subject, of 42, Mount Ararat Road, Richmond, Surrey, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

- The present invention relates to the manufacture of acetal condensation products.

- It is known that di-acetals of the formula  $R.O.CH.O.CH.O.R$ , in which "R"



- stands for the methyl or ethyl group, can be prepared by reacting bis- (Alpha chlor ethyl) ether with a solution of metallic

sodium in methanol or ethanol (Geuther and Laatsch, Ann. 218, 1883, page 25).

It is an object of the present invention to produce poly-acetals by which term are to be understood compounds of the general formula

$C_2H_5O.[CH(CH_3)O]_n.C_2H_5$  in which "n" is a numeral higher than 1, in particular 2 and 3, in a simple and less circuitous manner.

The process of the invention for the manufacture of poly-acetals comprises interacting a mixture of acetal and acetaldehyde at a temperature between plus 20° and minus 50° C. by the addition of a catalytic amount of an acid substance.

As acid substances may be used mineral acids such as hydrogen halogenides, for instance hydrochloric acid or hydrobromic acid, sulphuric acid or mono alkylated sulphuric acids, such as methyl hydrogen sulphate. The quantity of acid to be added can vary and depends partly on whether the intention is to produce the di-acetal, the tri-acetal or higher acetals, and also on the temperature in the reaction mixture. The higher the tempera-

ture within the indicated limits the smaller can be the quantity of acid to be added. It has been found that at temperature above zero a trace of the acid is sufficient to produce the desired effect.

At the lower temperature as much as 0.5 mol per cent, based on whichever reacting component of the initial reaction mixture is present in the smaller quantity, may be used but in some cases, as little as 0.001 mol per cent or even less was found to be sufficient. It is desirable to add the acid diluted in an alcohol or an inert organic solvent for the acid in order to avoid too great an increase of temperature, as this may give rise to very violent reactions which might even assume an explosive character. As diluent for the acid such substances as ethyl ether or alcohol may be used with advantage. Thus, for instance, the hydrogen halides are applied dissolved in ethyl ether and the sulphuric acid diluted with ethanol or methanol. Care has to be taken, also, to cool the reaction mixture efficiently in order to maintain the temperature within the desired range. The molar ratio of acetal to acetaldehyde may also vary within wide limits; ratios of acetal to aldehyde from 2:1 to 1:6 may for instance be used. A predominance of acetaldehyde will lead to the preferential formation of polyacetals higher than the tri-acetal which is also favoured by effecting the reaction at the lower temperatures within said range, that is between  $-10^{\circ}$  and  $-50^{\circ}$  C. A molar ratio of acetal to acetaldehyde of 2:1, on the other hand, leads to the production of a mixture which contains more di-acetal than tri- and poly-acetals.

When the reaction was carried out at temperatures of  $-50^{\circ}$  C. and lower, it was found that with the formation of the polyacetals increasing quantities of the auto-condensation products of acetaldehyde were formed. Small amounts of these latter substances were formed besides the production of poly-acetals when the reaction was carried out according to the process of the invention.

The separation of the polyacetals from metaldehyde, paraldehyde and unreacted acetal and acetaldehyde can be carried out by fractional distillation after the reaction mixture has been neutralised. The diacetal boils at  $156.5$  to  $158.5^{\circ}$  C. at ordinary pressure, whilst the triacetal has a boiling point of  $84$  to  $89^{\circ}$  C. at 5 mm pressure and a refractive index  $n_D^{20} = 1.4087$ .

The following examples illustrate the manner in which the process of the invention may be carried out in practice.

#### EXAMPLE 1.

Freshly distilled acetal (b.p.  $103-104^{\circ}$  C. was mixed in equimolecular proportion with freshly distilled acetaldehyde and to 500 cc. of the mixture cooled to  $-45^{\circ}$  C. was added 0.01 mol % of sulphuric acid (based on the initial acetaldehyde) diluted with methanol. The reaction mixture was kept at  $-45^{\circ}$  C. for two hours, then neutralised and subjected to fractional distillation. 28% of the initial acetaldehyde were converted to di-acetal and tri-acetal and 9.3% to paraldehyde and metaldehyde.

#### EXAMPLE 2

Acetal and acetaldehyde were mixed in a molar proportion of 2:1. 0.1 mol % of methyl hydrogen sulphate (based on the initial acetaldehyde) diluted with methanol was added at  $-20^{\circ}$  C. After two hours and treatment as indicated in Example 1, 40% of the acetaldehyde were converted to di-acetal and poly-acetal.

#### EXAMPLE 3

When 0.1 mol % of methyl hydrogen sulphate was added to a mixture, as used in Example 2, at a temperature of  $15^{\circ}$  C. di-acetal in a yield of 15% (based on the initial acetaldehyde) was obtained after  $\frac{1}{2}$  hour.

#### EXAMPLE 4

To a mixture of one mol of acetal and 6 mols of acetaldehyde was added 0.002 mol % of methyl hydrogen sulphate (based on the initial acetal) diluted with methanol at a temperature of  $-40^{\circ}$  C. After  $1\frac{1}{2}$  hours and neutralisation the reaction mixture yielded on fractionation 16.9 cc of a mixture boiling between  $128^{\circ}$  C. and  $180^{\circ}$  C. and consisting mainly of di-acetal and some tri-acetal, and 15.0 cc of a poly-acetal of the above given general formula, wherein "n" is 3 and greater than 3.

The poly-acetals produced according to the process of the invention may be used, e.g. as froth flotation agents and as organic intermediates.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of poly-acetals as hereinbefore defined which comprises interacting a mixture of acetal and acetaldehyde at a temperature between plus  $20^{\circ}$  and minus  $50^{\circ}$  C. by the addition of a catalytic amount of an acid substance.

2. Process according to Claim 1, wherein the acid substance is a mineral acid.

3. Process according to Claim 1, wherein the acid substance is a mono alkyl ester of sulphuric acid.
- 5 4. Process according to Claim 1, 2 or 3, wherein the amount of said acid substance is a trace when the reaction is effected at temperatures above  $0^{\circ}\text{C}$ .
- 10 5. Process according to Claim 1, 2 or 3, wherein the amount of said acid substance is between 0.5 and 0.001 mol per cent calculated on the amount of reacting component in the reaction mixture which is present in the smaller quantity, when the reaction is effected at temperatures below  $0^{\circ}\text{C}$ .
- 15 6. Process according to any preceding claim, characterised in the application of the acid substance diluted in an alcohol or an inert organic solvent for said acid substance.
- 20 7. Process according to any preceding claim wherein the molar ratio of acetal to acetaldehyde in the reaction mixture is from 2:1 to 1:6.
- 25 8. Process according to Claim 7, wherein a ratio in which acetaldehyde predominates is used for the production of polyacetals higher than the tri-acetal.
9. Process according to Claim 8, wherein the reaction is effected at temperatures within the range of minus  $10^{\circ}$  and minus  $50^{\circ}\text{C}$ .
10. Process according to Claim 7, wherein the molar ratio of two acetal to one acetaldehyde in the reaction mixture is used for the preferential production of di-acetal.
11. Process according to any preceding claim, wherein the polyacetals are recovered by neutralising and fractionally distilling the reaction mixture.
12. Process for the manufacture of polyacetals as hereintofore defined substantially as described in examples 1, 2, 3 or 4.
13. Polyacetals when produced by any of the processes claimed in Claim 1-12.
- Dated this 24th day of October, 1949.
- N. F. BAKER,  
Agent for the Applicants.

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